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SUPERCONDUCTING TUNNELING AND TUNNELING APPLICATIONS IN HIGH TC--ETC(U)
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(6) SUPERCONDUCTING TUNNELING AND TUNNELING APPLICATIONS IN HIGH T_c A15 SUPERCONDUCTORS.

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I. INTRODUCTION

This program was an outgrowth of our early empirical successes in forming superconducting tunnel junctions on thin films of the high transition temperature superconductors,[1] specifically those in the so-called A15 class such as Nb_3Sn ($T_c \cong 18$ K) and V_3Si ($T_c \cong 16$ K). Prior to this all attempts at tunneling in the A15 superconductors had been on bulk material and were not widely successful. Moreover such non-thin film junctions are of limited device interest. As a result of this program we now have general junction formation techniques, apparently suitable for the A15 superconductors as a class, which are being routinely used for material diagnostics and for studies of the superconducting properties of these materials.[2] More importantly, perhaps, they appear to have important device potential.[3] A general review[4] of advanced superconducting materials for electronic applications based on this work has been prepared for publication as an invited paper in the IEEE Transactions on Electron Devices and is included as an appendix to this report. Consequently, here we summarize only the main results and conclusions, refering the reader to the appendix for a more comprehensive discussion.

II. SUMMARY OF THE RESULTS

The program evolved along four major and interrelated lines:

(1) Development of Procedures for Forming the A15 Compound Base Electrodes and Insulating Tunnel Barriers

Using electron beam coevaporation we have established the optimal deposition conditions for the base electrodes. In general we find slow ($\sim$ 1 nm/sec) depositions on the hottest substrates ($T \gtrsim 700°C$) compatible with the phase

diagram of the material seem to produce the highest quality, well-ordered material with good superconducting properties. We have also found that thin (~ 30 Å) amorphous silicon layers deposited in situ on the base electrodes and subsequently oxidized form excellent tunneling barriers (with a Pb counter-electrode) on all the A15 superconductors with which it has been tried.[5] A model for the behavior of this barrier has been developed which explains its success and detailed behavior, and also provides guidance as to under what conditions it should be applicable.[5] We have also shown that in the particular case of Nb_3Sn the native oxide can also yield very good tunnel junctions.[6] In fact the civility of the oxide of Nb_3Sn compared to that of Nb metal itself, along with a variety of circumstantial evidence, suggests that excess Sn on the surface plays an important role in the favorable properties of the oxide. Moreover the demonstration that the presence of a *non-transition-metal can so markedly affect the oxidizing* behavior of a transition metal alloy or compound suggests the possibility that it may be easier to form tunnel junctions with Nb- or V-alloys generally than with the pure elements (which historically have presented great difficulties).

(2) Study of the I-V Characteristics of the Junctions as a Material Diagnostic

With our junctions we can now routinely study the effects of composition,[2] applied magnetic fields,[7] etc. on the energy gap of the superconductor. One particularly important result (Ref. 7) of this sort is the demonstration that Nb_3Sn can have a very large surface barrier to flux entry — a feature of considerable current importance in potential high-power rf applications. Also the quality (i.e. extremely low leakage) of the barriers we form is now good enough that non-idealities in the tunneling characteristic can be associated with the properties of the base high-T_c superconducting electrode rather than

the barrier. For example the presence of second (non-superconducting) phases is readily detected by virtue of the associated excess tunneling current below the superconducting energy gap. Thus phase diagrams of the materials of interest can be established and study of the role of second phases in stabilizing the A15 phase in the high-T_c metastable A15's such as Nb_3Al, Nb_3Ge and Nb_3Si appears feasible in this way.

(3) Careful Analysis of the Data from the Best Junctions to Obtain the Electron-Phonon Interaction Spectral Function $\alpha^2(\omega)F(\omega)$.

The detailed information available from good tunnel junctions about the electron-phonon interaction responsible for superconductivity is unrivaled by any other measurement. We have extracted this information for our best Nb_3Sn junctions. The analysis reveals the phonon structure clearly but is not free of the historical problem in tunneling studies of the transition metals that the strength of the phonons is not strong enough to account for the superconductivity (e.g. Δ and T_c) without yielding a so-called "negative μ^*" (i.e. an attractive electron-electron Coulomb interaction).[8] Such results are controversial and we have recently applied the proximity tunneling model approach of Arnold and Wolf to our data in an attempt to resolve this question.[9] The approach yields a positive μ^* but is not free of controversy itself. Further research will be required before this issue is settled definitively one way or the other.

(4) Study of the Josephson Tunneling Behavior and its Device Potential

This very important aspect of our work is described in detail in Ref. 4, which also forms the appendix of this report. Suffice it here to say that the Josephson properties of our Nb_3Sn/Pb junctions exhibit excellent figures of merit as regards gap values (high), leakage currents (low),

dielectric constant of the oxide barrier (low), magnitude of Josephson current (in accord with theory), and mechanical properties (robust). The importance of these results lies in the fact that these junctions hold the promise of combining both good electrical and mechanical properties — a combination not found in the more highly developed Pb/Pb and Nb/Pb tunneling Josephson junction technologies. We emphasize, however, that smaller, higher current density junctions must be demonstrated with our devices before they can be considered for practical applications. Also because of the fragility of the thin tunneling barriers, the fabrication of an all high-T_c Nb_3Sn/Nb_3Sn tunnel junction remains problematical and some form of weak-link Josephson device still remains the best hope for a high-T_c Josephson technology.

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PERSONNEL

Several graduate students, post-doctoral researchers, and visiting scientists have participated in the research accomplished under this program. They are listed below along with their present place of employment.

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7. "Fabrication and Barrier Diagnostics of Superconductive Tunnel Junctions On Nb-Sn and V-Si," by D. A. Rudman, R. E. Howard, D. F. Moore R. B. Zubeck, and M. R. Beasley, IEEE Trans. Mag. MAG-15, 582 (1979).

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9. "Oxidized Amorphous-Silicon Superconducting Tunnel Junction Barriers," by D. A. Rudman and M. R. Beasley, to appear in Appl. Phys. Lett.

10. "Advanced Superconducting Materials for Electronic Applications," by M. R. Beasley, to appear in the IEEE Transactions on Electron Devices on Superconductive Junctions.

APPENDIX

ADVANCED SUPERCONDUCTING MATERIALS FOR ELECTRONIC APPLICATIONS

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ABSTRACT

Recent progress in the fabrication of tunnel junctions with the high-T_c transition-metal compound and transition-metal alloy superconductors is reviewed. The potential advantages of these materials for practical applications are described and their special problems assessed. It is found that, based on work to date, Nb_3Sn may have practical device potential.

I. INTRODUCTION

While there are literally thousands of superconducting materials known, when it comes to electronic applications the number of interest reduces considerably. This reduction reflects the demanding requirements dictated by the need for materials that not only can be used to make good Josephson junctions but that are also compatible with integrated circuit processing. These requirements have been discussed in detail in the preceeding articles on Pb alloys [1] and Nb [2]. Chief among these are: a large superconducting energy gap Δ (and consequently a high transition temperature T_c) to ensure well developed superconductivity at practical cryogenic temperatures; a high-quality metal-oxide tunneling barrier (or suitability for use of some deposited barrier material) with a low dielectric constant to provide good,

controllable tunneling characteristics and low device capacitance; and good mechanical properties in order to withstand the thermo-mechanical stresses associated with thermal cycling between room and cryogenic temperatures. Also desirable are a superconducting coherence and magnetic penetration lengths that are large and small respectively. The former governs the distance scale over which the properties of the superconducting material must be maintained homogeneous to avoid degrading the superconducting properties, and the latter governs the extent to which magnetic fields penetrate the superconductor and puts a lower limit on the physical thickness of the various superconducting circuit elements. Finally, to minimize difficulties in processing one desires materials that are not sensitive to impurities or damage and that can be processed at room temperature.

As discussed in Ref. 1 the present technological front runner are the Pb-In-Au and Pb-Bi alloys developed at IBM for use in their Josephson computer technology. Tunnel junctions formed with these materials have excellent electrical characteristics but are mechanically soft. Unfortunately it is the soft nature of Pb-alloy tunnel junctions that is the root problem in obtaining long life under thermal cycling, specifically the shorting of the tunnel junctions by stress induced incipient hillock formation [3]. Next comes Nb, which has a higher transition temperature ($T_c \approx 9.2$ K) and excellent mechanical properties (even with a Pb counter electrode) but which remains lacking in its electrical characteristics. The dielectric constant of the oxide tunneling barrier (Nb_2O_5) is very large (leading to excessive device capacitance), and the I-V characteristics frequently show nonidealities in the form of excess conduction at voltages below the energy gap, despite considerable effort at improvement [2]. This excess conduction limits the output current the junction can switch and results in

marginal device gain. It is the need for superconducting materials that yield Josephson junctions with simultaneously good electrical and mechanical properties, and the desire for devices capable of higher operating temperatures, that has motivated work on advanced superconducting materials for electronic applications.

The classes of superconducting materials with the greatest hope for meeting these needs are the transition-metal compounds, particularly those of the A15 (e.g., Nb_3Sn, $T_c \simeq 18$ K) or B-1 (e.g., NbN, $T_c \simeq 16$ K) crystal structures, or possibly the transition-metal alloys. These materials have the highest transition temperatures (up to 23K) and the good mechanical properties of refractory metals, although it should be noted that the compounds are somewhat brittle. The best superconducting properties are found in those compounds and alloys based on Nb or V.

Although the Nb- and V-based transition-metal compounds and alloys have many attractive features, their use presents problems as well. Since they incorporate at least two constituents and do not diffuse readily except at elevated temperature, the production of thin films of these materials requires precise codeposition of some type. Moreover, because these materials have very short superconducting coherence lengths (typically $\lesssim 50$ Å), for tunneling applications the films must be of excellent quality right up to the surface since it is the top coherence length of material that determines the tunneling characteristic. In the case of the compounds the superconducting properties are sensitive both to stoichiometry and crystallographic order.

To achieve good order requires deposition at elevated temperatures ($T_s \simeq 600 - 1000^{o}C$) or a high temperature anneal of some kind. The sensitivity of the superconductivity of these materials to order, combined with their short coherence lengths, also places some serious constraints on fabrication procedures such as surface cleaning. Finally, like Nb itself, in general these materials are subject to the idiosynchratic chemistry of the transition metals. Nevertheless progress has been made recently, spurred by advances in codeposition of the refractory, high-T_c superconductors that has made good thin films of these materials available for the first time. Some very good Josephson junctions have been produced, and it is the objective of this review to summarize this work and to identify the problems and prospects for the future.

II. THIN-FILM DEPOSITION TECHNIQUES AND FILM PROPERTIES

As mentioned above a crucial factor in making possible even consideration of the transition-metal compounds and alloys for electronic applications has been recent advances in the thin film deposition of these materials. Earlier work aimed at forming tunnel junctions with these compounds and alloys in bulk form has not been widely successful and is not suitable for integrated circuit applications in any event. Table 1 lists all of the superconducting materials with transition temperatures comparable to or higher than Pb (7.2 K) or Nb (9.2 K) with which thin film tunnel junctions have been reported. Also listed are the deposition technique and conditions employed to make the films.

By far the most widely applied deposition scheme has been dual-electron-beam coevaporation. The development and application of this technique for the high-T_c, A15-type superconductors was pioneered by Hammond [4]. Sputtering

from composite targets has also been successfully employed in some cases, most notably Nb_3Ge, which in sputtered films has the highest transition temperature of any superconductor known [5,6,7]. In the main, however, the flexibility of multi-electron-beam codeposition has proved to be a great asset at the present research stage. Electron beam codeposition affords good control over deposition rate, chemical composition (hence stoichiometry) and can be used to grade composition near the surface or possibly deposit artificial barriers for tunnel junctions. When arranged in the so-called phase- (or composition-) spread configuration, it allows production of a series of samples with varying chemical composition in a single deposition. Hammond [4] has reviewed the application of e-beam codeposition to superconducting materials research, and a schematic of the evaporator built by Hammond and presently in use at Stanford University is shown in Fig. 1.

The deposition conditions (rates, substrate temperature, etc.) required to produce good superconducting films varies from material to material as indicated in Table I. The optimal conditions for tunnel junction formation have not been studied exhaustively, but Nb_3Sn has received a good deal of attention and will be discussed in Section III. In general, however, it appears that for the transition-metal compounds slow deposition (e.g., ~ 1 nm/sec) on the hottest substrate temperature possible compatible with the phase diagram of the material and film thickness not exceeding ~ 0.5 μm consistently produce the best tunneling results. Films produced in this way have good superconducting properties (e.g., T_c's) and within single phase regions are very smooth with good growth morphologies (fine columnar grains; highly textured) and well ordered [8]. The A15 superconductors that are metastable at the stoichiometric ratio of 3:1, such as Nb_3Al and Nb_3Ge, present special problems, however [6,7,9]. Thicker films can have good superconducting properties but

tend to be too rough for good tunneling. Films in two phase-regions generally are less satisfactory because of poorer growth morphologies and because the second phase invariably is a poorer superconductor or fully normal material, which results in increased conduction below the gap and also leakage due probably to tiny metallic shorts in the junctions. Detailed studies of the growth morphologies of evaporated thin films of the A15 superconductors can be found in Reference 10.

The alloy films are in the main easier to make and require only that two phase regions are avoided and that the films be kept thin enough. Amorphous superconducting films have received relatively little attention [11] but are of considerable interest becuase of their great homogeneity and good mechanical properties. To date only one preliminary study of tunneling on NbN has been reported, although it is an obvious candidate and has been made very successfully in thin film form [12]. It is also believed to be less damage sensitive than the A15-type superconductors.

III. TUNNELING RESULTS

A. A15-Compounds

The first tunnel junction formed on an A15 superconducting film was reported by Moore, et al [13]. They used air oxidized Nb_3Sn films deposited using the techniques of Hammond. The counter electrode was Pb. Subsequently many other A15 compounds have been successfully incorporated into junctions as evidenced by the entries in Table I. However, of all these materials only Nb_3Sn has been studied in detail to date, and in our subsequent discussion we shall be largely concerned with this material. The junction geometry typically employed is illustrated in Fig. 2 where it is seen that the barrier may be the native oxide or an oxidized amorphous

silicon (a-Si) layer.

Following their initial success, Moore, et al. [8], investigated the optimal deposition conditions for producing good tunnel junctions and the properties of the resultant junctions as a function of composition. It was found that the best results were obtained at the highest substrate temperature possible consistent with the volatility of Sn and for very slow deposition rates. Typical values were ~ $800^{o}C$ and 1- 3 nm/sec, respectively. The high substrate temperature presumably ensures good ordering in the material. The low rate should also promote ordering but apparently also ensures that the top layer of the film is not affected by compositional transients when the main evaporation shutter is closed. Since, as mentioned above, the top 50 Å or so of the film determine the tunneling behavior, it is absolutely essential to ensure it is of the highest quality. Background pressures in the evaporator (typically ~ 10^{-7} torr) were not found to affect junction quality markedly.

Typical tunneling I-V characteristics as a function of composition across the A15 phase field (18-25% Sn) are shown in Fig. 3. As seen in the figure, on the whole the I-V curves are quite good with small leakage and conduction below the gap and a fairly sharp rise at the sum of the energy gaps $\Delta_{Pb} + \Delta_{Nb-Sn}$. The origin of this width in the rise of the I-V curve is not presently understood, although it presumably represents gap anisotropy. As the Sn concentration increases up to ~ 25% Sn (<u>i.e.</u>, up to Nb_3Sn), the energy gap Δ_{Nb-Sn} increases. Beyond 25% Sn a two-phase region (Nb_3Sn + Nb_6Sn_5) is entered and the gap remains high but the leakage in the junction I-V below the gap increases. (See the I-V curve for the 29% Sn junction.) This leakage arises due to presence of second phase material in the films in the form of protruding inclusions of Nb_6Sn_5. Films in this region have a frosty appearance. The frequency of

shorts in the tunnel junctions also increases the further one enters this two-phase region. Figures 4 and 5 show the composition dependence of the gap Δ and T_c for the Nb-Sn system. As expected the best superconducting properties occur at stoichiometry. Note, however, that outstanding junctions often are obtained just slightly into the two-phase region. Under these conditions the films are very homogeneous and reproducible (with only a very few second-phase inclusions) even if the evaporation is uneven across the film.

In attempting to extend their work to V_3Si, Moore, et al [14], found that it was necessary to deposit a thin amorphous silicon (a-Si) layer on the top V_3Si surface, which was subsequently oxidized to form the tunneling barrier, in order to obtain good tunneling. As illustrated in Fig. 6, the effect of the oxidized a-Si barrier on the quality of the I-V curves is profound. The native oxide invariably gave very poor tunneling curves and very large junction resistances. Progressive improvement in the I-V curve and a systematic reduction in the junction resistance was noted as the thickness of the a-Si was increased up to $\sim$ 2 nm. For larger thicknesses the tunneling remained good and the junction resistances once again increased. Subsequently it has been found that oxidized a-Si barriers work equally well (and with extremely good reliability) on all the other A15 superconductors, including Nb_3Sn [8], Nb_3Al [15], and Nb_3Si [16], with which it has been tried. With these a-Si barriers the tunneling results obtained with V_3Si were very similar to those shown in Figs. 3- 5 for Nb_3Sn [8] .

Recently Rudman and Beasley [17] have systematically studied the properties of these oxidized a-Si barriers on various materials and as a function of the thickness d_{Si} of the a-Si layer. They found that for the 20-hour

air oxidation used in their work, universally the best tunneling was obtained at $d_{Si} \simeq 2$- 3 nm. They also found that the specific resistances of the junctions decreased and ultimately converged to a universal value of ~ 0.01 $(\text{mhos/cm}^2)^{-1}$ independent of the base electrode material as d_{Si} was increased from zero up to this optimal value. For larger d_{Si} the resistances were observed to increase exponentially, also in a universal manner, with a characteristic scale length of ~ 1 nm.

Based on their results Rudman and Beasley propose a model for these barriers in which the a-Si layers serve both to passivate the base electrode and to form a high-quality tunneling barrier. More specifically they suggest that in contrast to the case with no a-Si in which one gets good tunneling or not depending on the particular base electrode, when a thin a-Si layer is deposited, the oxide barrier consists of SiO_x and some native metal oxide underneath. The I-V curves are improved and the junction resistance decreases, but the native oxide still has some influence on the tunneling behavior. (For example, see Fig. 6 .) When the optimal thickness is reached, the a-Si layer is oxidized all the way through but the base electrode remains unoxidized. This leads to good tunneling because of the good barrier properties of SiO_x and the junction conductance becomes independent of the base electrode. For larger Si thicknesses an unoxidized a-Si layer remains under the SiO_x and results in the exponentially increasing junction resistance with d_{Si} .

As demonstrated by Rudman and Beasley, however, using Au base electrodes (with which shorts were observed), these oxidized a-Si barriers do have pin holes, and their success on the A15 superconductors depends critically on the native oxide of the base electrode being sufficiently

resistive to successfully block the pin holes. Despite this limitation the technique has proved to be extremely useful with the A15-type superconductors. At present the conductances of these barriers are too low to be suitable for practical applications as Josephson junctions, although the Josephson effect is definitely present.

The Josephson properties of these Nb_3Sn/Pb tunnel junctions incorporating both native oxide barriers and oxidized a-Si barriers were first studied by Howard, et al. [18]. Their most remarkable result was that the specific capacitance of the junctions (even using the native oxide) were considerably lower than those found with Nb/Pb junctions. An I-V curve showing the dc Josephson current is shown in Fig. 7. The specific capacitance ϵ/t of the barrier and the magnetic field penetration depth λ of the Nb_3Sn base electrode as determined from the Josephson magnetic field dependent quantum interference pattern and the junction electromagnetic resonances steps (Fisk modes) are shown in Fig. 8 as a function of composition. The penetration depths observed ($\sim 0.1 - 0.2$ μm) are not extremely small but certainly suitable for applications. The specific capacitances ($\sim 2\mu F/cm^2$) found are very small, however, roughly a factor of four smaller than that reported for Nb/Pb junctions [19]. Another remarkable feature of these junctions was that good tunneling could be obtained even after the base electrodes had been subjected to photolithographic processing to define the junction area before depositing the Pb counter electrode. The good I-V characteristics observed with these junctions combined with their favorable dielectric constants, apparent tolerance to processing, and anticipated good mechanical properties has quickened the interest in A15 superconductor Josephson junctions, even with Pb counter electrodes.

Because of the favorable preliminary results obtained with Nb_3Sn/Pb junctions, additional work has been undertaken to better understand their properties, why they work so well, and in particular why they appear to work better than Nb. The low value of the specific capacitance ϵ/t obtained from the Fisk mode analysis clearly indicates that the oxide involved is not simply Nb_2O_5 as is generally believed to be the case with pure Nb. Moreover, preliminary Auger analysis on one of the films used in these tunneling studies indicated the presence of excess Sn on the surface. Further circumstantial evidence for the involvement of Sn oxides was obtained by Rudman et al [20]. These authors noted that an inadvertent source of excess surface Sn — reevaporation of Sn onto the film surface from the surrounding furnace after the main evaporation was terminated — was probably present in the earlier tunneling work by Moore, et al. Nevertheless even when every precaution was taken to minimize Sn reevaporation onto the film, Rudman and co-workers found that outstanding tunnel junctions could still be obtained providing that the appropriate oxidation atmosphere was employed. Figure 9 shows their results. As seen in the figure, as the oxidizing atmosphere progressed from dry air to room air and then from humid air to a saturated vapor pressure of acetic-acid in air, the tunneling characteristics improved dramatically. The curves shown are only for Nb 20 % Sn but are representative of the systematics seen at all compositions as well. The important role of humidity in tunnel junction oxide barrier formation has been noted by Garno [21]. Also the beneficial effects of oxidization in acetic acid vapor in the case of In tunneling barrier formation have been shown by Hebard and Arthur [22]. Subsequent work showed the acetic acid did not have such a beneficial effect on pure Nb, however [23]. Once again the Sn is implicated, but in this case it is not yet clear how much Sn is on the surface nor through what mechanism it may have gotten there.

Further information about the oxidation of Nb_3Sn is available from the Auger and UPS study of the oxidation of bulk Nb_3Sn by Strozier et al. [24] and by Miller [25]. According to Miller, unlike Nb, the oxide of Nb_3Sn is diffusion limited and, not surprisingly, contains both Nb_2O_5 and SnO_2. More importantly perhaps, he concludes it is apparently free of the deep penetration of Nb sub-oxides (NbO and Nb_2O) that are believed to be the likely origin of many of the problems encountered in Nb junctions. Miller attributes this lack of oxygen diffusion to the presence of the Sn oxide although no precise mechanism is proposed. In any event even though a complete understanding of oxide barrier formation on Nb_3Sn is still lacking, it is quite clear that its behavior is fundamentally different (and better for tunneling) than that of pure Nb. We shall return to an assessment of the practical implications of these results on Nb_3Sn tunnel junctions in Section IV.

Of the other A15 superconductors shown in Table I none has been as successful nor received as much attention as Nb_3Sn. Some good tunneling curves have been reported [6, 15] but none yet of the quality of that seen in Fig. 7. The Josephson effect is generally present, but its associated material parameters have not been established. Of all the A15 superconductors V_3Si is probably the easiest to make and deserves more attention from the practical point of view, although its future would appear to be closely tied to that of the a-Si barriers. Nb_3Al and Nb_3Ge are very much harder to make because of their metastability. They are of great scientific interest, however, and so one can expect progress will be made in both their synthesis and tunneling. The reader is refered to the original references for information on the detailed status of junctions on these materials.

B. Alloys

Surprisingly very little tunneling work has been reported on transition metal alloy films with T_c's above that of Pb. The reasons are not entirely clear and may represent proprietary interests, or perhaps simply reflect the greater current scientific interest in the higher T_c transition metal compounds. Of the tunneling work reported on alloys most of it has apparently been motivated by interest in amorphous materials. The most complete report of the Josephson properties was reported by Yeh and Tsuei [26] for Nb-Al/Pb junctions. Both crystalline and amorphous alloys were formed. The study was motivated in part by the hope that the Al in the alloy would promote good oxide barrier formation. This was apparently not borne out unless an additional layer of pure Al ($\sim$ 2nm thick) was deposited on the surface prior to oxidation. The junctions with the oxidized Al layers yielded some good junctions with low leakage, Josephson current densities up to 1000 A/cm^2, penetration depths of the Nb-Al alloy of $\sim$ 1200 Å, and dielectric constants a factor of 6 less those pure Nb. The two other stable amorphous alloys with good T_c's for which tunneling has been reported are a-$Mo_{30}Re_{70}$ and a-$Mo_{.8}N_{.2}$ [11]. The Josephson behavior of these materials was apparently not studied in detail. Crystalline films of Nb-Ti alloys have also been made and yielded tunnel junctions, although their properties have not yet been studied [27].

IV. CONCLUSIONS

Clearly none of these advanced materials is yet suitable for serious consideration in applications. On the other hand only a few years ago no one would have thought the progress would have been a great as it has

been. Such an assessment was based on the chronic problems exhibited by Nb . It is now clear, however, that there are some real advantages in going beyond this elemental transition metal to the compounds and alloys. Clearly Nb_3Sn has emerged as an interesting prospect deserving further development. In particular one needs to establish whether all of its demonstrated favorable figures of merit can be achieved simultaneously. Moreover, it has yet to be shown that junctions with sufficiently high current densities to be of practical interest can be made at all. Finally, barrier formation techniques compatible with integrated circuit processing may be hard to establish unless some means for cleaning the surface of this damage sensitive material can be developed. Of the other A15 superconductors only V_3Si is presently sufficiently advanced to warrant careful study of its behavior from the practical Josephson junction point of view. The transition metal alloys appear to be essentially unexplored. It will be interesting to see whether they develop as nicely as the A15 compounds. Certainly they would be easier to use in practice because of their damage insensitivity and low substrate deposition temperatures.

Artificial barriers are hardly new, but the utility of the oxidized a-Si barriers observed with the A15 superconductors is certainly unprecedented. The demonstration of a barrier that works and whose properties are independent of the base electrode certainly must be considered significant. Such deposited barriers may be hard to control, however, and the implications of the pin holes have not been fully assessed or even empirically investigated. The existence of a model for the behavior of these barriers should now hasten progress in this area.

One final point is that to date all the junctions on these advanced materials have employed Pb as the counter electrode. While this by

no means precludes their practical interest, ultimately one would like to have mechanically hard counter electrodes as well — not to mention hard, high-T_c counter electrodes. Neither of these will be easy, although the former can at least be imagined at the present time. Nb/Nb junctions can be made (although not with outstanding characteristics) and there seems no reason why Nb or a Nb alloy couldn't be used as a counter electrode on the materials discussed in this paper. What deterioration in electrical characteristics might accrue is not yet known, however. At the present time the need to deposit the transition metal compound superconductors at high substrate temperatures seems to preclude making the top electrode of a tunnel junction from these materials. Thus short of some new way of ordering these superconductors without either a conventional high temperature deposition or anneal must probably be developed before tunnel junctions incorporating all high-T_c materials will be possible. Consequently one must presently still look to weak-link microbridge-type Josephson junctions as the most likely route to high-T_c devices [28,29].

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TABLE I

Thin-Film Deposition Conditions for Tunnel Junction Fabrication on Transition-Metal Compounds and Alloys

Material	T_c [K]	Crystal Structure	Deposition Technique	Substrate	Substrate Temperature [°C]	Deposition Rate [nm/s]	Reference
Nb_3Sn	17.8	A15	e-beam	sapphire	700 - 800	1 - 3	8
V_3Si	16.3	A15	e-beam	sapphire	700 - 800	1 - 3	8
Nb_3Ge*	23	A15	sputtering/ e-beam	sapphire	750 - 900	0.1-1.5	6,7,8
Nb_3Al*	16.7	A15	e-beam	sapphire	750 - 1000	1 - 9	9
Nb-Al	up to 8K	bcc/ amorphous	e-beam/ sputtering	Si and sapphire	LN_2 - 150	1	26
Nb-Ti	9-10 K	bcc	e-beam	sapphire	~ 100	1	27
a-$Mo_{.8}N_{.2}$	8.3	amorphous	reactive e-beam	--	LN_2	--	11
a-$Mo_{.3}Re_{.7}$	8.6	amorphous	sputtering	--	LN_2	--	11

*For these metastable A15 superconductors various means are used to stablize the A15 phase such as impurity stabilization, self-epitaxy, and polycrystalline epitaxy.

FIGURE CAPTIONS

Fig. 1. Schematic of electron-beam coevaporator. Three independent electron-beam heated sources, each feedback controlled with evaporation rate monitors, can be used to codeposit up to three elements simultaneously and to deposit subsequent layers for artificial tunnel barrier formation or for insulation layers. For phase-spread orientation the substrate holder is rotated 90 degrees. Mechanical mask can be used for defining junction areas during insulator deposition and/or complete insitu junction fabrication. Not shown is a furnace for heating substrates. [Courtesy R. Hammond].

Fig. 2. Typical junction geometry. Barriers can be native oxide or oxidized a-Si layers. Dielectric insulators can be hand-painted "Q-dope", deposited insulators, or photoresist. In all reported work to date the counter electrode has been Pb .

Fig. 3. I-V curves as a function of composition for the Nb-Sn system across the A15 phase field. The 29% Sn curve is in a two phase region and shows the increased leakage generally observed when significant second phase inclusions are present. The variation of the I-V's with composition is typical of the A15 compounds and shows that the behavior systematically improves as stoichiometry is approached. Curves were taken at 1.5K. [From Ref. 8].

Fig. 4. Variation of energy gap of the Nb-Sn system across the A15 phase field. Behavior typical of the A15 compounds generally. Note break in behavior at the phase boundary, which occurs essentially at $\approx$ 25% Sn, i.e. at Nb_3Sn . [From Ref. 8].

Fig. 5. Variation of T_c of the Nb-Sn system across A15 phase field. Note Δ and T_c follow some trends. Vertical lines indicate width of the transition as measured inductively. This width is believed to reflect compositional variations across the 1/4" x 1/4" films used in the measurements. Films were deposited in phase-spread configuration. Note break in behavior at the phase boundary as in Fig. 4. [From Ref. 8].

Fig. 6. Typical I-V curves for V_3Si showing effect of increasing thickness of a-Si barrier layers. [From Ref. 8].

Fig. 7. I-V curve of Nb_3Sn/oxide/Pb junctions showing Josephson effect. Expanded scales show leakage conductance below energy gap. Note that this particular junction was oxidized using acetic acid vapor as described in text and is "typical" of the better junctions. [From Ref. 21].

Fig. 8. Compositional dependence of the specific capacitance ε/t and the magnetic field penetration depth λ across the Nb-Sn system. Data determined from measurement of junction magnetic diffraction pattern of the critical current and ac Josephson effect junction resonances (i.e. Fisk modes). [From Ref. 18].

Fig. 9. I-V curves for Nb-Sn/oxide/Pb tunnel junctions prepared using different oxidizing atmospheres. Junctions were typically $0.3 \times 0.9\ mm^2$. Oxidation time was 20 hours. [From Ref. 21].

CONSTANT COMPOSITION SUBSTRATE ORIENTATION

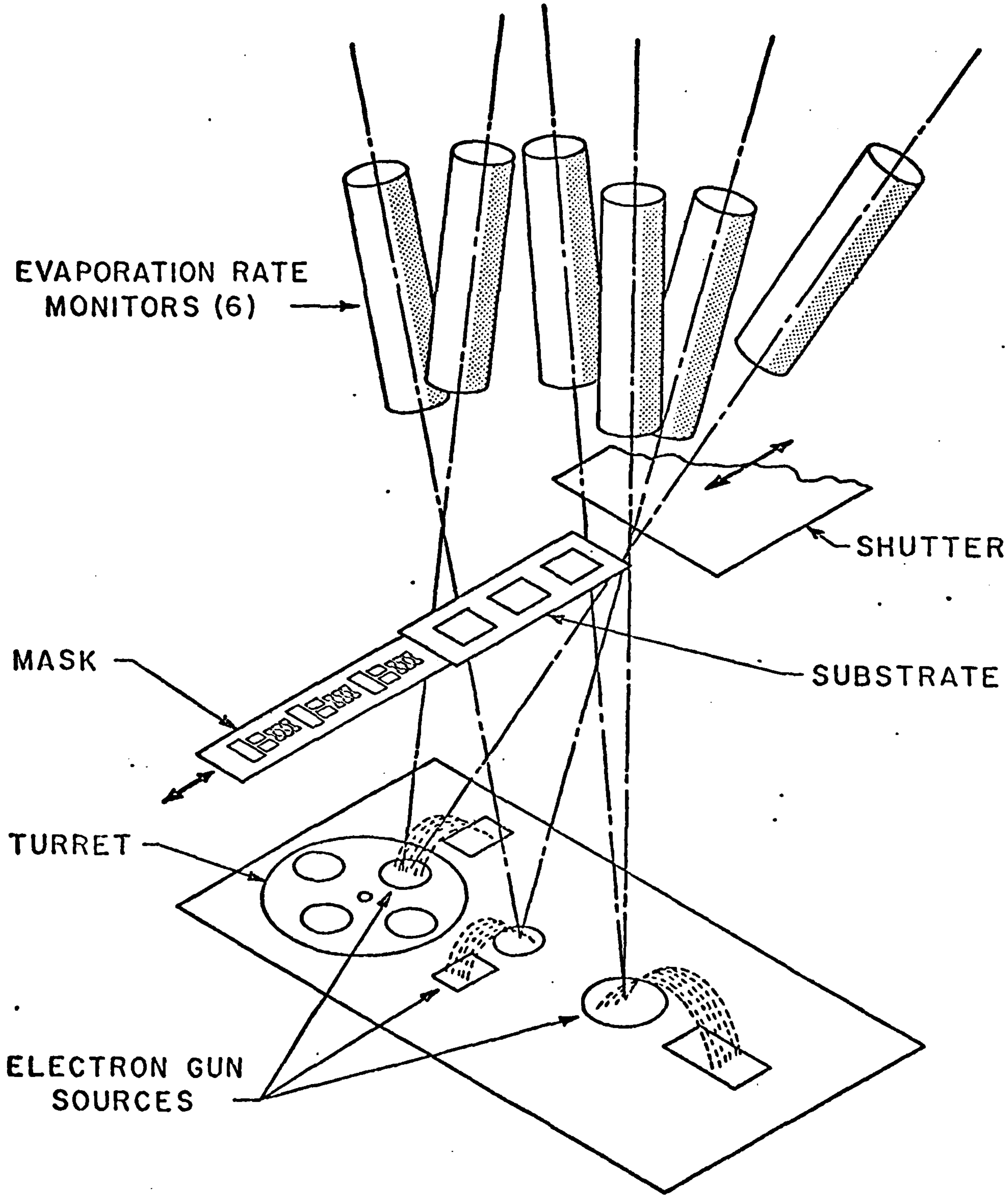


Fig. 1

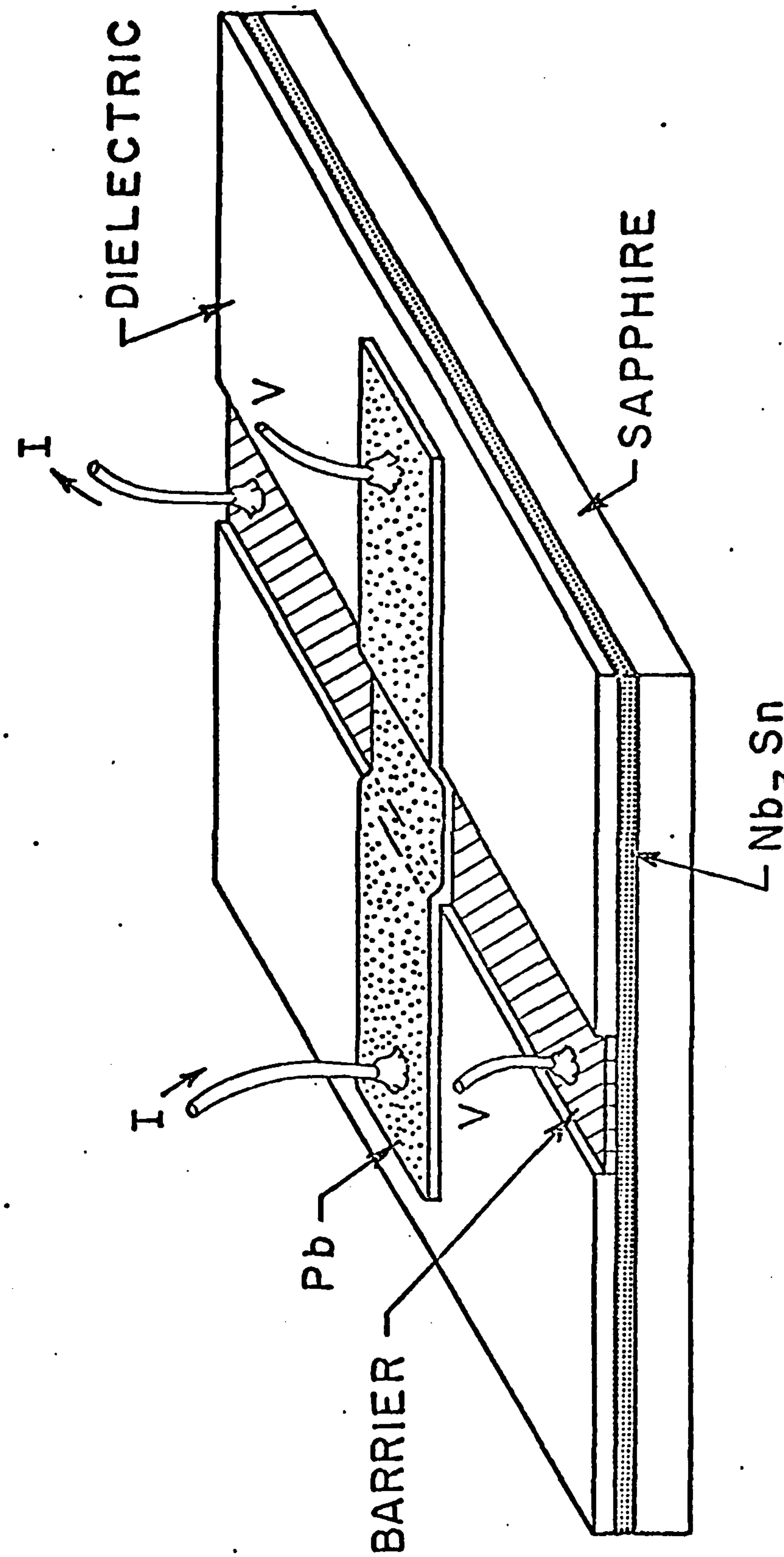
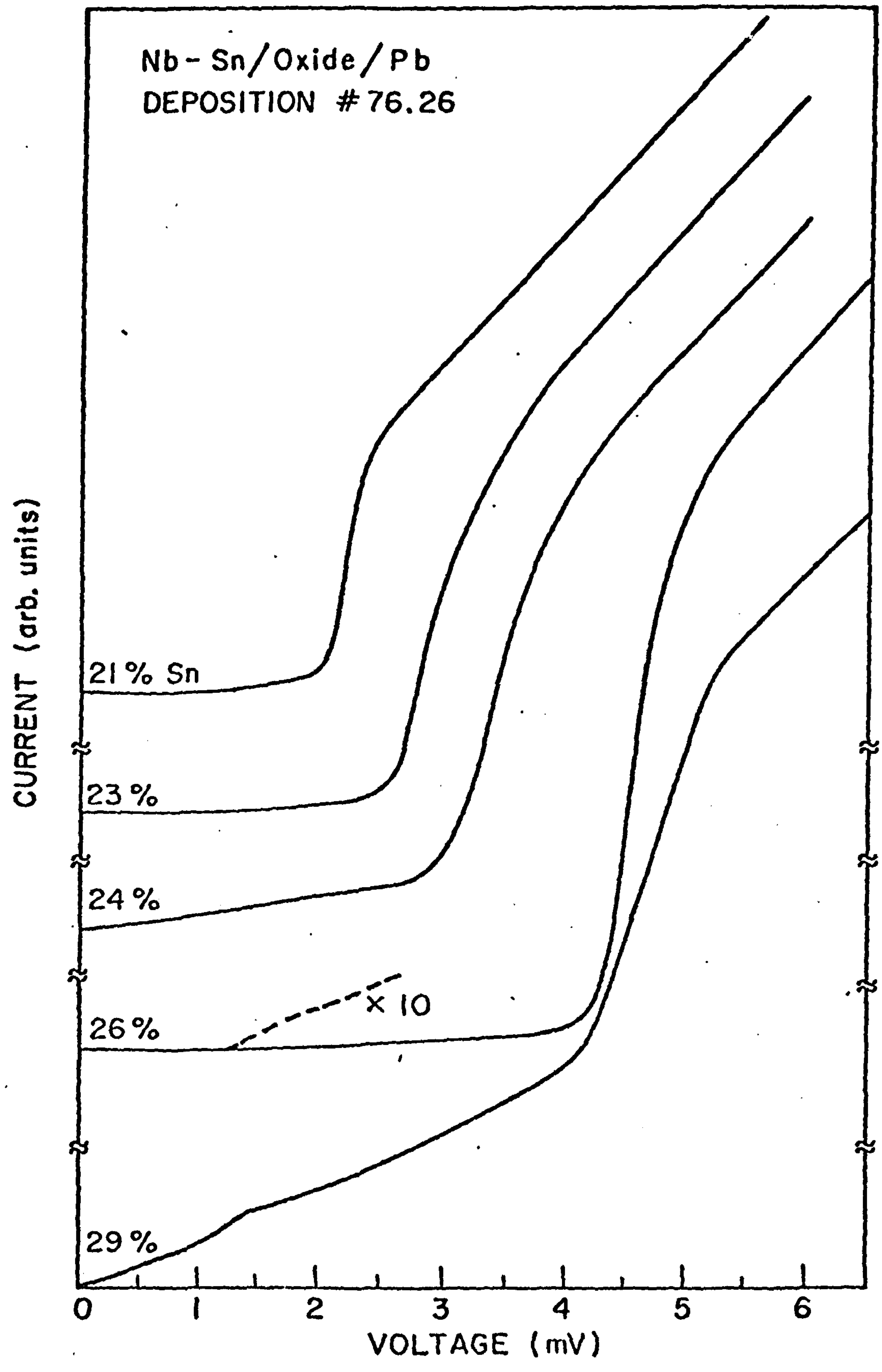


FIG. 2



Nb-Sn/Oxide/Pb
DEPOSITION #76.26
CURRENT (arb. units)
21% Sn
23%
24%
26%
×10
29%
0
1
2
3
4
5
6
VOLTAGE (mV)

FIG. 3

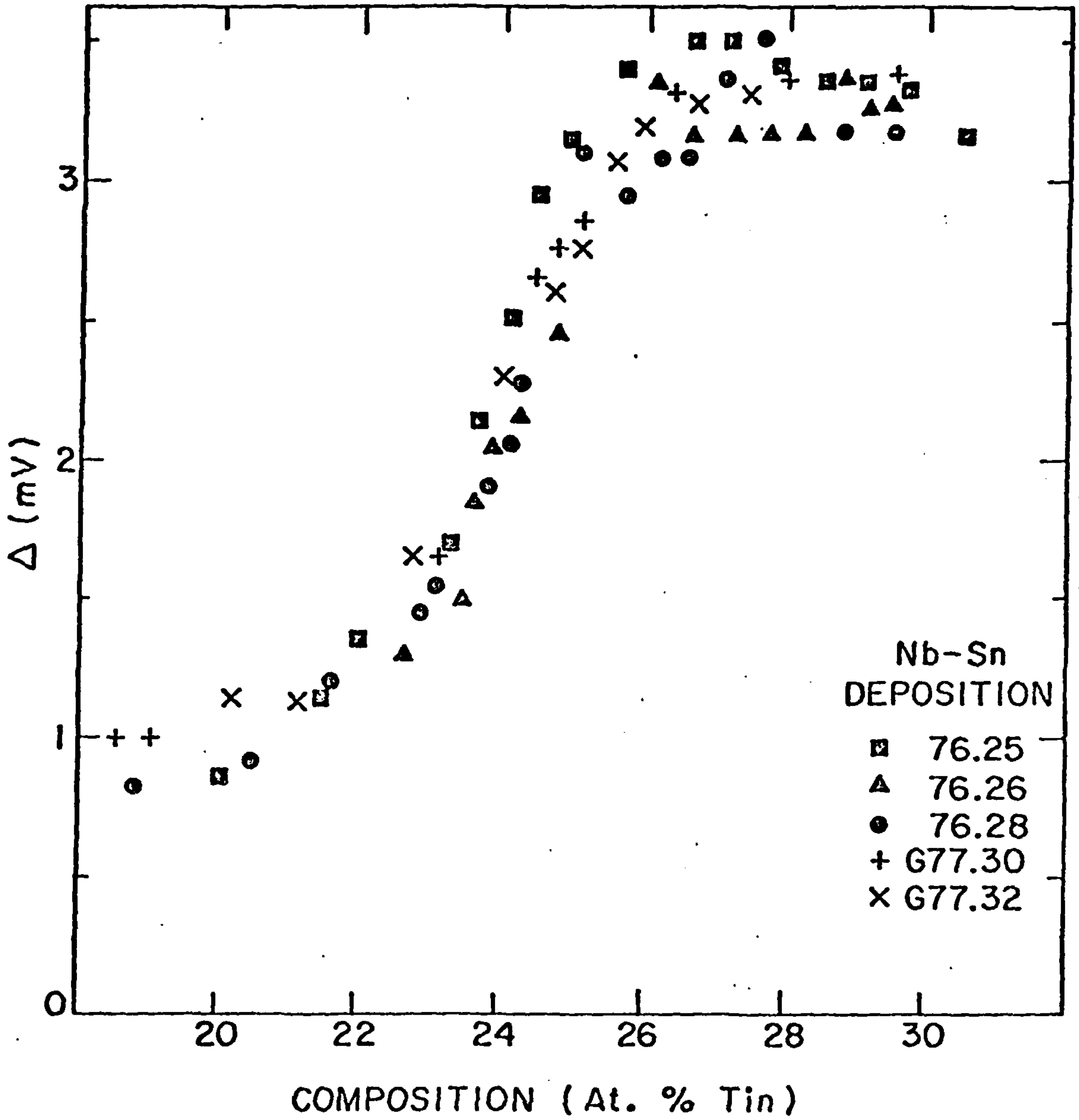
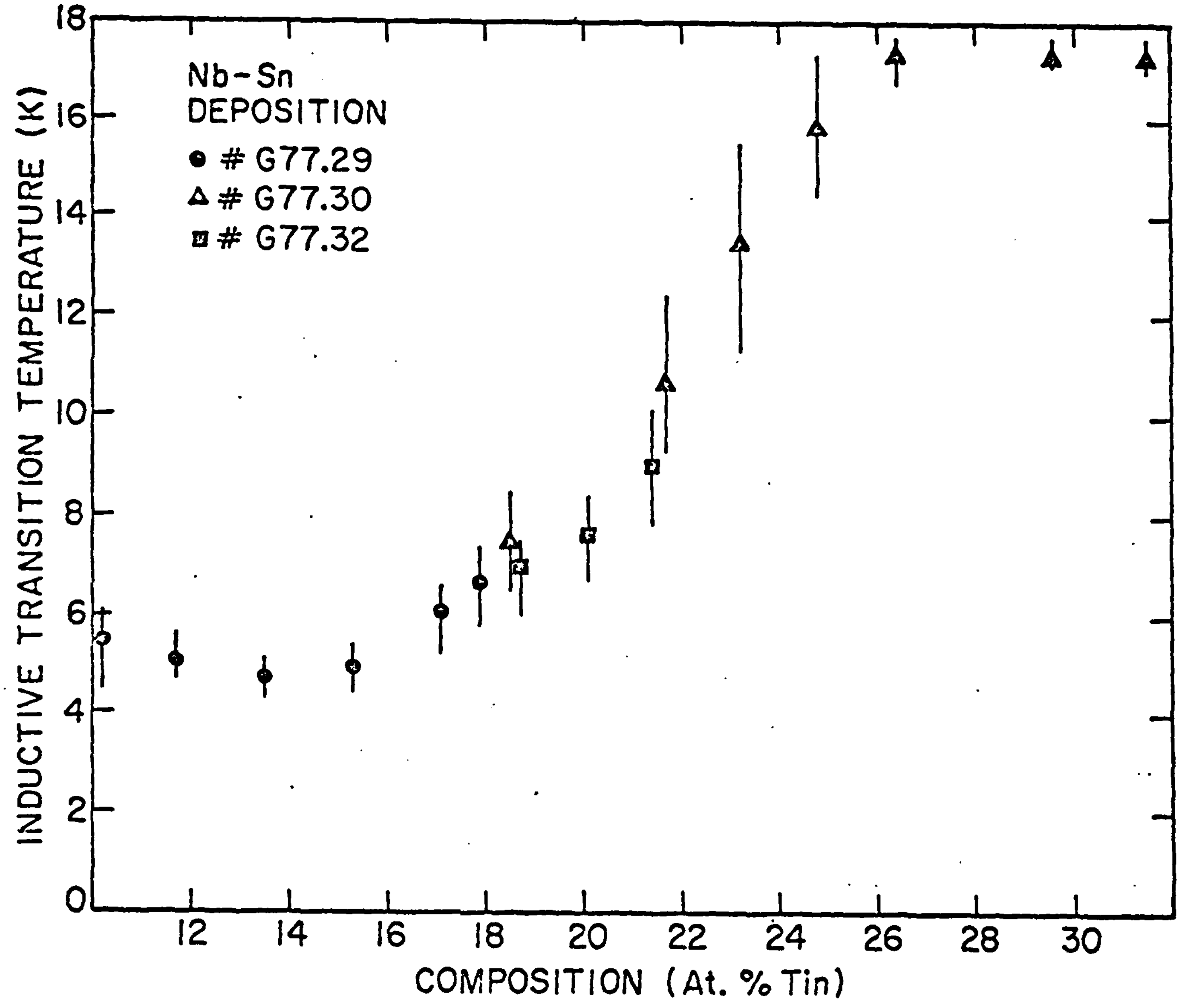

Δ (mV)
0
1
2
3
20
22
24
26
28
30
COMPOSITION (At. % Tin)
Nb-Sn
DEPOSITION
76.25
76.26
76.28
G77.30
G77.32

FIG. 4



Nb-Sn
DEPOSITION
G77.29
G77.30
G77.32
INDUCTIVE TRANSITION TEMPERATURE (K)
COMPOSITION (At. % Tin)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

FIG. 5

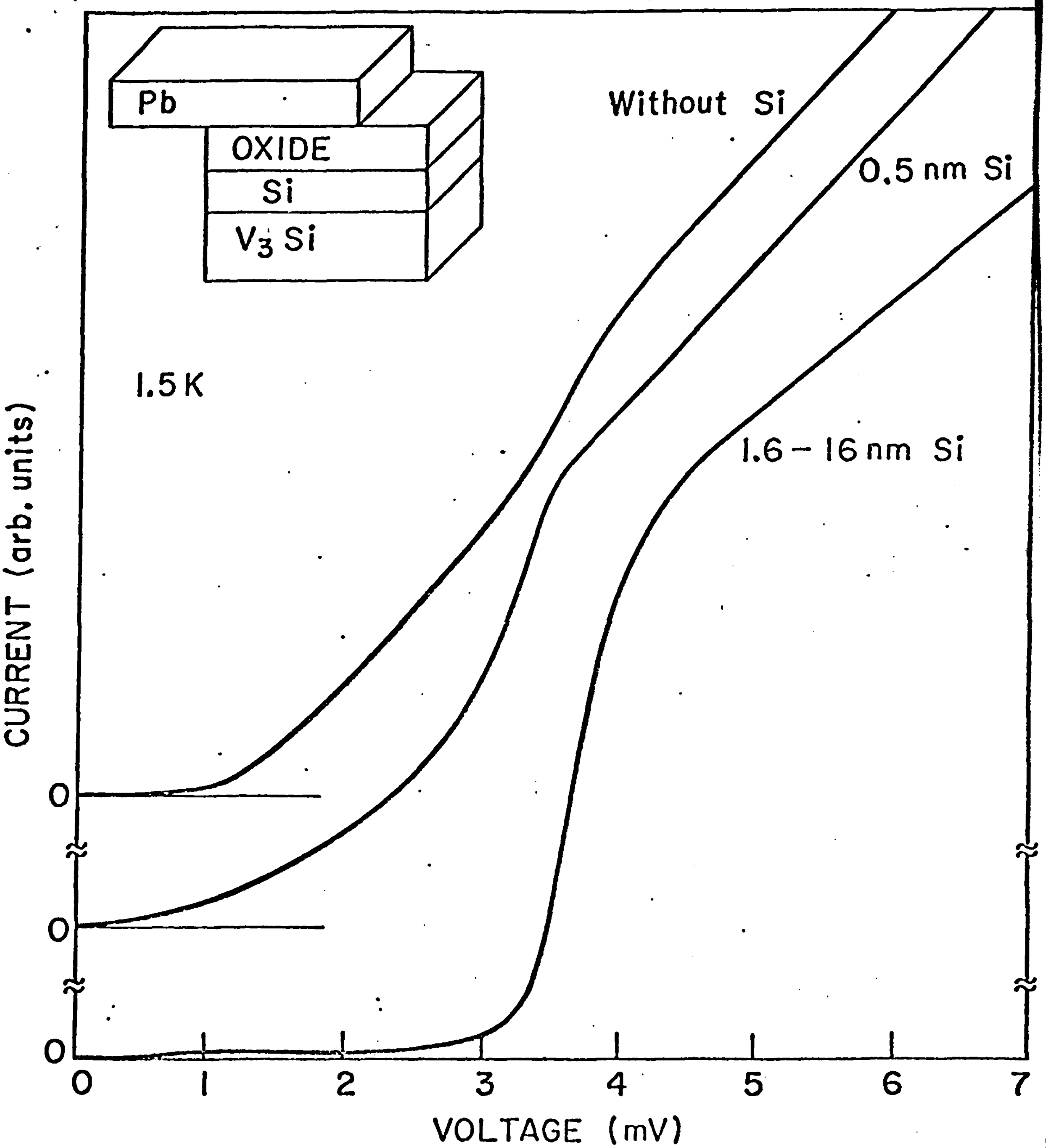

Pb
OXIDE
Si
V_3 Si
Without Si
0.5 nm Si
1.6 - 16 nm Si
1.5 K
CURRENT (arb. units)
0
0
0
0
1
2
3
4
5
6
7
VOLTAGE (mV)

FIG. 6

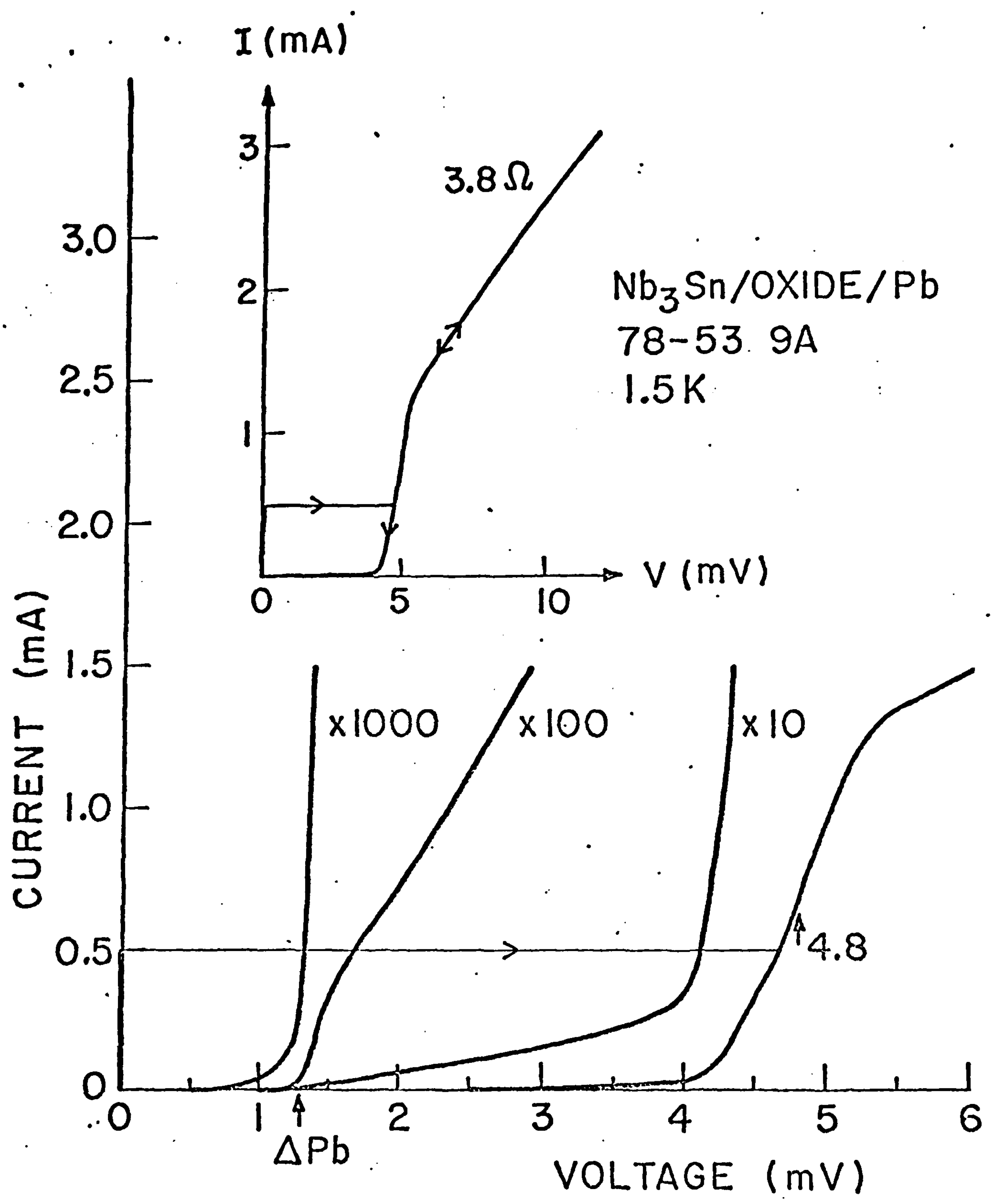
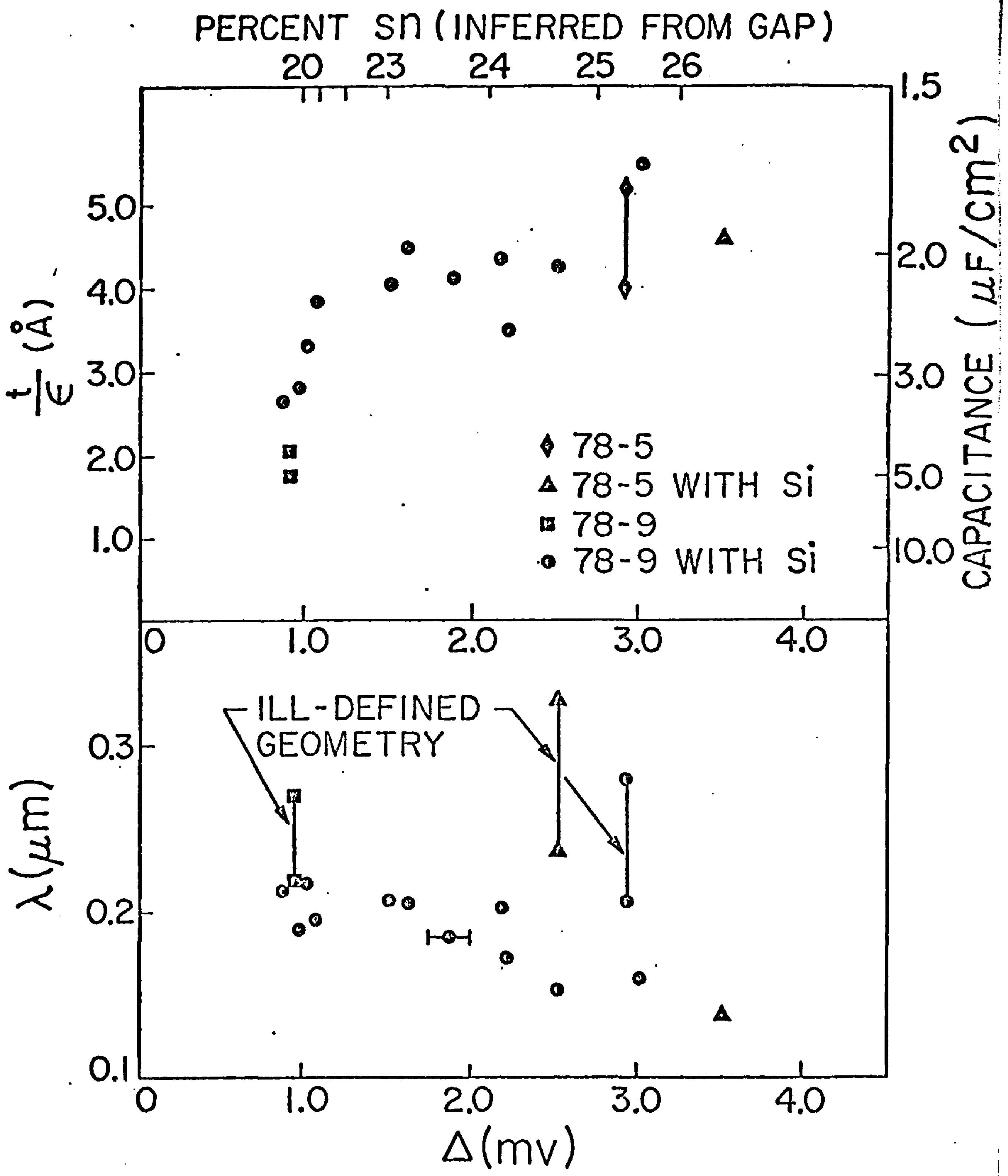

I (mA)
3
2
1
0
5
10
V (mV)
3.8 Ω
Nb_3Sn/OXIDE/Pb
78-53 9A
1.5 K
CURRENT (mA)
3.0
2.5
2.0
1.5
1.0
0.5
0
x1000
x100
x10
4.8
0
1
2
3
4
5
6
ΔPb
VOLTAGE (mV)

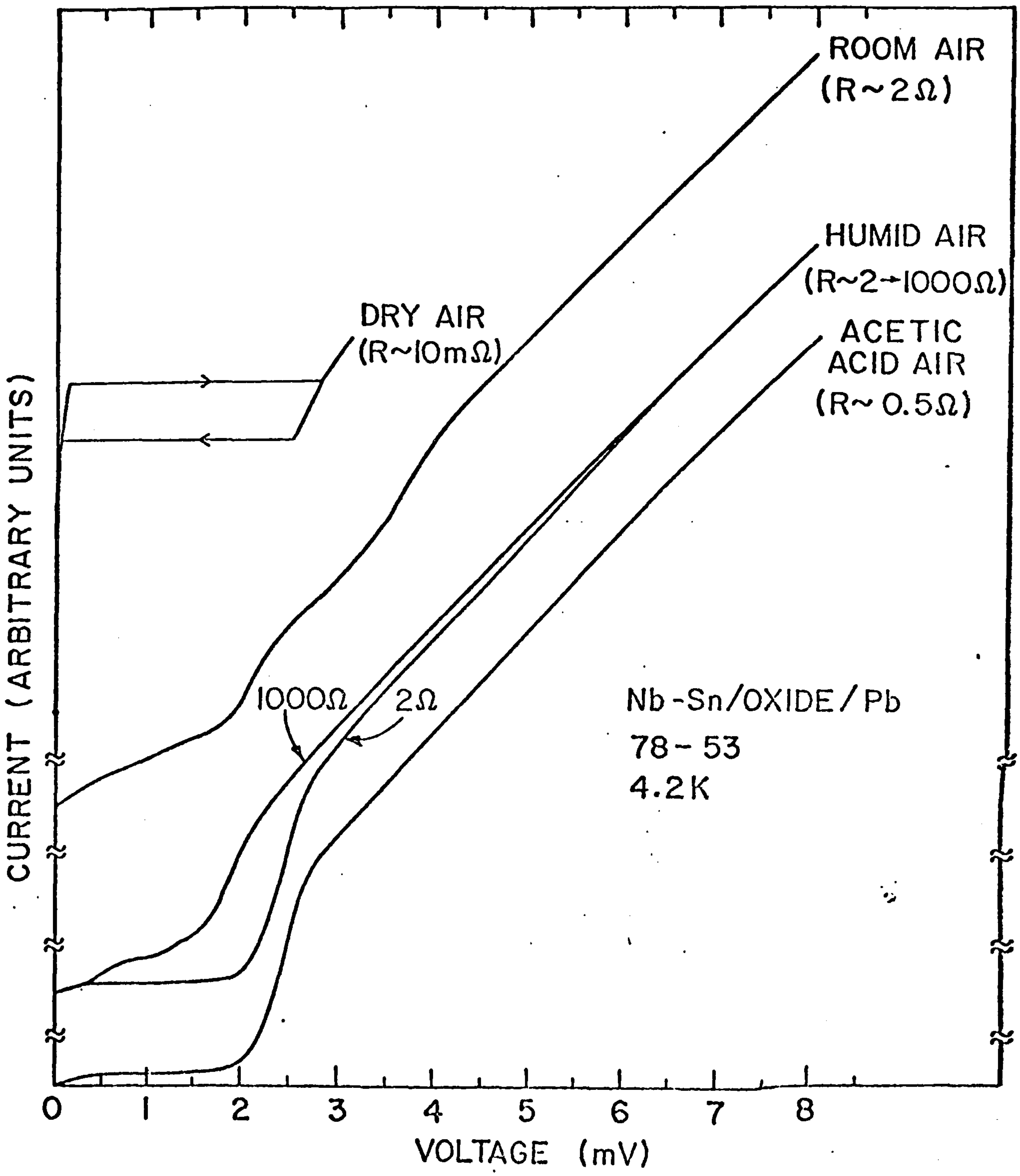
FIG. 7



PERCENT Sn (INFERRED FROM GAP)
20
23
24
25
26
1.5
2.0
3.0
5.0
10.0
CAPACITANCE (μF/cm^2)
5.0
4.0
3.0
2.0
1.0
$\frac{t}{\epsilon}$ (Å)
78-5
78-5 WITH Si
78-9
78-9 WITH Si
0
1.0
2.0
3.0
4.0
ILL-DEFINED GEOMETRY
0.3
0.2
0.1
$\lambda(\mu m)$
0
1.0
2.0
3.0
4.0
Δ(mv)

FIG. 8

4024-1



ROOM AIR
(R~2Ω)
HUMID AIR
(R~2→1000Ω)
DRY AIR
(R~10mΩ)
ACETIC
ACID AIR
(R~0.5Ω)
1000Ω
2Ω
Nb-Sn/OXIDE/Pb
78-53
4.2K
CURRENT (ARBITRARY UNITS)
0
1
2
3
4
5
6
7
8
VOLTAGE (mV)

FIG. 9